



## High-temperature vapour–liquid equilibrium for the (water + alcohol) systems and modelling with SAFT-VR: 2. Water-1-propanol

A.F. Cristino<sup>a</sup>, S. Rosa<sup>a</sup>, P. Morgado<sup>b</sup>, A. Galindo<sup>c</sup>, E.J.M. Filipe<sup>b</sup>, A.M.F. Palavra<sup>b</sup>, C.A. Nieto de Castro<sup>a,\*</sup>

<sup>a</sup> Departamento de Química e Bioquímica and Centro de Ciências Moleculares e Materiais, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

<sup>b</sup> Departamento de Engenharia Química e Biológica and Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

<sup>c</sup> Department of Chemical Engineering and Centre for Process System Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

### ARTICLE INFO

#### Article history:

Received 8 November 2012

Received in revised form 20 December 2012

Accepted 21 December 2012

Available online 7 January 2013

#### Keywords:

1-Propanol

Water

Mixtures

VLE

SAFT-VR EOS

### ABSTRACT

Accurate vapour–liquid equilibrium (VLE) measurements of binary mixtures involving water and linear aliphatic alcohols, an important alternative source of energy, are needed for the design of industrial processing of these compounds. In this paper, VLE measurements for the (water + 1-propanol) system were carried out over the temperature range 403.2 K to 423.2 K and pressures up to 0.72 MPa using a flow apparatus.

The Statistical Associating Fluid Theory for potentials of Variable Range (SAFT-VR) was used to model the system. The experimental results are accurately reproduced with this approach, using binary interaction parameters slightly modified from those previously used for the (water + ethanol) system.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

The design of many processes in Chemical Engineering needs the knowledge of the thermophysical properties of fluids [1–3]. During the last 30 years, a great effort has been spent in the experimental programmes to measure the vapour–liquid equilibria (VLE) of binary mixtures. There are a many of these experimental studies at low and room temperatures [4,5]. However, the situation is rather different at high temperatures.

Biodegradable fuels are playing an important role in the world global economy, as oil prices are increasing steadily. The search for alternative energies and new fuels is vital for the sustainability of the world economy. The production of biodegradable fuels needs accurate measurements on (water + alcohol) systems, such as methanol, ethanol, propanol and butanol (linear and branched) at high temperatures. So, these VLE measurements have become one of the key factors for the design of industrial plants for the process of these new fuels.

Recently, a VLE experimental program at high temperatures was developed in a collaboration between the Experimental Thermodynamics Laboratory (CQE-IST) and Centre for Molecular Sciences and Materials (CCMM-FCUL). The VLE measurements over the temperature range 363.3 K to 423.7 K have been performed for the system (ethanol + water) [6] using a flow apparatus. The

next step involves the measurements of the (C<sub>3</sub> + water) systems, from which 1-propanol is the natural start, although its production in industry is more complicated than that of 2-propanol. Nevertheless, the interest in separating the contributions of the interactions between linear aliphatic chains and water, trying to understand the structural changes in liquid water due to the addition of the alcohol molecule, justify our choice.

To the best of our knowledge, there are only two sets of data for the system (water + 1-propanol). Ratcliff and Chao measured the *P*(*x*,*y*) diagram at *T* = 363.15 K [7]. On the other hand, Adrien *et al.* [8] studied the ternary system CO<sub>2</sub> + water + 1-propanol at *T* = (303, 313 and 333) K, for pressure between 5.5 and 16.1 MPa. These authors did not find any immiscibility gap for the binary mixture (water + 1-propanol) at the temperatures and pressures studied.

From a theoretical point of view, a major step in our understanding of liquids and liquid mixtures has been the development of molecular-based equations of state (EOS), such as the SAFT equation [9–11]. Unlike typical engineering or cubic equations of state, SAFT explicitly takes into account the contribution of molecular details, such as non-sphericity (molecular shape), polarity and association. In this work, we have used SAFT-VR, which describes molecules as homonuclear chains of hard-core monomers that interact through attractive potentials of variable range, typically a square well, [12,13]. This potential has been successfully used to describe the phase equilibria of a wide range of industrially important systems (see reference [14] and the references therein).

\* Corresponding author.

E-mail address: [cacastro@fc.ul.pt](mailto:cacastro@fc.ul.pt) (C.A. Nieto de Castro).

**TABLE 1**

Purity of liquids.

Compound	Supplier	Mass fraction purity or equivalent	Purification
Water	Lab Production (Milli-Q)	Resistivity 180 kΩ·m	Deionised and degassed before use
1-Propanol	Fisher Scientific	>0.999	Dried with anhydrous copper sulphate
Tetrachloroethylene	H&D Fitzgerald (Certified)	>0.990	Density Certified ampoules

An experimental study of this system was performed in our laboratory at temperatures 403.2 K, 413.2 K, and 423.2 K and pressures up to 0.72 MPa, with the flow apparatus previously described [6].

The VLE equilibrium is achieved inside a high pressure cell. Within this cell, the temperature is measured using a calibrated Pt100 resistance thermometer. The pressure was measured with two pressure transducers. The equilibrium compositions of both phases were determined using vibrating tube densimetry. This apparatus was fully tested with experimental values obtained for the (water + ethanol) system [6].

The experimental results for the (water + 1-propanol) was modelled using the SAFT-VR EOS.

## 2. Experimental

The VLE measurements were carried out using a flow apparatus which has been described in detail in a previous paper [6]. This apparatus operates over the temperature range 363 K to 443 K and pressures up to 1.7 MPa. The temperature is measured with a platinum resistance thermometer with an uncertainty of 0.1 K, while the pressure is read using two pressure transducers with ranges of 0–0.4 MPa and 0–1.7 MPa with uncertainties of 0.0002 MPa and 0.0009 MPa, respectively.

The 1-propanol was supplied by Fisher Scientific with a confirmed mass fraction purity greater than 0.999 and the water was distilled and deionised in a Millipore apparatus (Milli-Q) with a resistivity of 180 kΩ·m (see table 1). As 1-propanol is highly hygroscopic, a glass vessel with anhydrous copper sulphate was placed before the sample glass vessel of the flow apparatus.

The liquid and vapour phase composition were determined indirectly by densimetry, calibrated according the methodology described by Lampreia and Nieto de Castro [15]. Densities were measured with an Anton Paar DSA 5000 M densimeter calibrated with water and tetrachloroethylene with an expanded uncertainty of 0.01 kg·m<sup>-3</sup> ( $k = 2$ ). Tetrachloroethylene was supplied by H&D Fitzgerald with confirmed mass fraction purity greater than 0.99 and density values certified (see table 1). Furthermore, the calibration curve as a function of composition (third order polynomial of the molar function of 1-propanol) was obtained from published data [16]. Using this analytical method the uncertainty of the molar function determination is 0.0001.

## 3. Theory

A quantitative interpretation of the results was performed using the molecular-based statistical associating fluid theory for potentials of variable attractive range, SAFT-VR, which has been successfully used to describe the phase behaviour of a wide range of systems, from simple molecules to complex multicomponent mixtures [17].

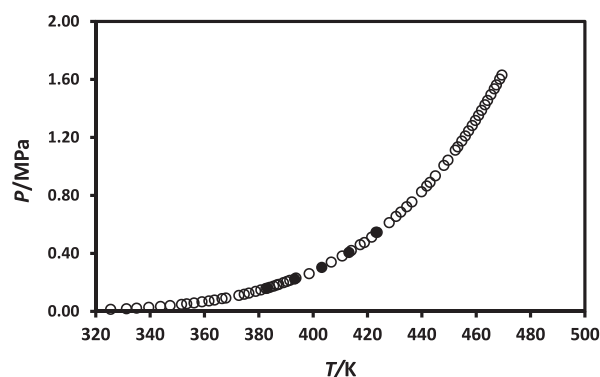
In the SAFT-VR approach, molecules are modelled as chains of  $m$  tangentially bonded hard spherical segments, with the attractive dispersive interactions described by a potential of variable attractive range such as the square-well potential used in this work. Each segment is characterized by three parameters, namely, the hard-sphere diameter  $\sigma$  and the depth  $\varepsilon$  and width  $\lambda$  of the potential

**TABLE 2**Vapour pressures (in MPa) for 1-propanol at several temperatures.<sup>a</sup>

T/K	This work p/MPa	Literature <sup>b</sup> p/MPa
383.2	0.1604	0.1607
393.2	0.2233	0.2231
403.2	0.3031	0.3040
413.2	0.4066	0.4073
423.2	0.5461	0.5373

<sup>a</sup>  $u(T) = 0.1$  K,  $u(p < 0.4) = 2 \cdot 10^{-4}$  MPa,  $u(p > 0.4) = 9 \cdot 10^{-4}$  MPa, and  $u(x_1) = u(y_1) = 1 \cdot 10^{-4}$ .

<sup>b</sup> Calculated from Antoine equation reported by Susial *et al.* [21].



**FIGURE 1.** 1-Propanol vapour pressures at different temperatures: (○) Susial *et al.* [19]; (●) experimental data.

well. In the case of associating molecules, such as water and ethanol which are hydrogen-bonding, embedded attractive square-well sites are included in the model, defined by their bonding volume  $K_{ab}^{HB}$  and the depth of the attractive potential  $\varepsilon_{ab}^{HB}$ . The full expressions for the SAFT-VR equation of state can be found in the original references [12,13].

The molecular model parameters for the pure substances are determined by minimization of the differences between theoretical and experimental properties, normally the liquid density and vapour pressure. The model used here for 1-propanol has been developed by Patel [18] and the model for water has been optimized by Clark *et al.* [19].

Water is represented as a single spherical segment ( $m = 1$ ) with four associating sites, two representing the hydrogen atoms and two the lone electron pairs. For 1-propanol, one association site representing the hydroxyl hydrogen atom and two the oxygen lone electron pairs are included; in this case, the number of spherical segments is 1.8667, accounting for the elongated molecular shape. It should be noted that, both in the pure compounds and in the mixture, the associative interactions are only allowed between sites of different type, namely “hydrogen-type” sites can only interact with “electron-type” sites and vice versa.

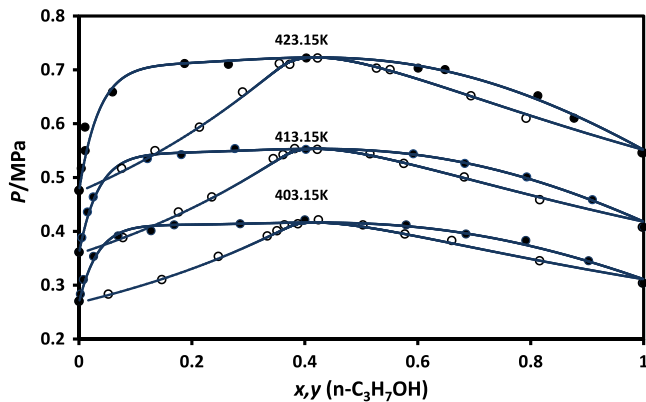
For the unlike interactions, pure arithmetic means have been used for the ranges and volumes, namely:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (1)$$

**TABLE 3**Vapour pressure of the (water + 1-propanol) system at  $T = (403.2, 413.2 \text{ and } 423.2) \text{ K}$ .<sup>a</sup>

$p/\text{MPa}$	$x_1$	$y_1$	$p/\text{MPa}$	$x_1$	$y_1$
$T = 403.2 \text{ K}$					
0.3042	0.9989	0.9981	0.4121	0.1686	0.3638
0.3455	0.9025	0.8158	0.4012	0.1277	0.3506
0.3832	0.7913	0.6601	0.3915	0.0692	0.3335
0.3952	0.6854	0.5771	0.3535	0.0259	0.2468
0.4121	0.5794	0.5029	0.3105	0.0078	0.1466
0.4215	0.4000	0.4240	0.2834	0.0024	0.0520
0.4141	0.2855	0.3876			
$T = 413.2 \text{ K}$					
0.4080	0.9993	0.9978	0.5538	0.2762	0.3820
0.4588	0.9093	0.8160	0.5426	0.1812	0.3614
0.5011	0.7950	0.6823	0.5351	0.1212	0.3441
0.5262	0.6832	0.5751	0.4640	0.0253	0.2352
0.5442	0.5921	0.5153	0.4361	0.0150	0.1761
0.5524	0.4018	0.4221	0.3884	0.0051	0.0778
$T = 423.2 \text{ K}$					
0.5461	0.9993	0.9974	0.7102	0.2646	0.3733
0.6102	0.8769	0.7918	0.7118	0.1870	0.3548
0.6520	0.8126	0.6941	0.6589	0.0594	0.2897
0.7004	0.6483	0.5509	0.5936	0.0106	0.2132
0.7033	0.6006	0.5267	0.5500	0.0110	0.1346
0.7221	0.4026	0.4226	0.5170	0.0041	0.0755

<sup>a</sup>  $u(T) = 0.1 \text{ K}$ ,  $u(p < 0.4) = 2 \cdot 10^{-4} \text{ MPa}$ ,  $u(p > 0.4) = 9 \cdot 10^{-4} \text{ MPa}$ , and  $u(x_1) = u(y_1) = 1 \cdot 10^{-4}$ .

**FIGURE 2.** Comparison between vapour-liquid equilibrium data of the present work (●, ○) and the application of the SAFT-VR theory (—) for water + 1-propanol system at several temperatures.

$$\lambda_{ij} = \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}}, \quad (2)$$

$$K_{ab,ij} = \left[ \frac{K_{ab,ii}^{1/3} + K_{ab,jj}^{1/3}}{2} \right]^3. \quad (3)$$

In order to describe quantitatively the mixture behaviour, the unlike dispersive and associative energetic parameters are normally modified from the usual geometric means by the introduction of adjustable correction factors ( $k_{ij}$  and  $k_{a,b,ij}^{HB}$ ):

$$\varepsilon_{ij} = (1 - k_{ij})(\varepsilon_{ii}\varepsilon_{jj})^{1/2}, \quad (4)$$

$$\varepsilon_{ab,ij}^{HB} = (1 - k_{a,b,ij}^{HB})(\varepsilon_{ab,ii}^{HB}\varepsilon_{ab,jj}^{HB})^{1/2}. \quad (5)$$

In the sequence of our previous work [6], we have used the same adjustable parameters ( $k_{ij} = -0.02297$  and  $k_{ij}^{HB} = 0.01989$ ), determined for the (water + ethanol) system [20], in order to obtain an absolute prediction of the vapour-liquid equilibria of (water + 1-propanol). It was found that the theory consistently over predicted the experimental vapour pressure of the mixtures. Quantitative agreement between the theoretical and experimental results was obtained by keeping the same associative cross-interaction and slightly adjusting the dispersive parameter to  $k_{ij} = -0.0290$ .

#### 4. Results and discussion

Vapour pressure data for pure 1-propanol over the temperature range 403.2 K to 423.2 K were obtained with the flow apparatus. A comparison of our results with calculated vapour pressures from the Antoine equation, using the same parameters than Susial *et al.* [21] is presented in table 2 and displayed in figure 1. The agreement is very good, well within the mutual uncertainty of the vapour pressure, except at the highest temperature, where our value is 0.01 MPa higher. The performance of the instrumentation was checked with pure water (see table 2 of Ref. 6) and the agreement with the IAPWS EOS [22], and no departure was found at this temperature. This departure can probably be explained by non-detected illness behaviour of the Antoine equation therein reported. Despite of this, our results were also compared with the experimental data of Susial *et al.* [21], and the agreement was found to be very good (figure 1).

Table 3 shows our experimental measurements for this system at the temperatures 403.2 K, 413.2 K and 423.2 K. Figure 2 shows the complete  $P(x,y)$  diagram at these temperatures. An azeotrope occurs for compositions around 0.4.

The results from the SAFT-VR equation of state, with the molecular model parameters used for water and 1-propanol displayed in table 4 are also presented in figure 2 along with the experimental values from this work. It should be stressed that to obtain the remarkable agreement displayed, the values of the binary interaction parameters were only slightly adjusted from those obtained for the (water + ethanol) system [20] and used in our previous work [6].

#### 5. Conclusions

The vapour pressure for pure 1-propanol was measured over the temperature range 403.2 K to 423.2 K. The results obtained attest to the good performance of our flow apparatus, as found previously for the (water + ethanol) system in similar conditions.

Experimental VLE results were obtained for the (water + 1-propanol) system at temperatures between 403.2 K and 423.2 K, and pressures up to 0.72 MPa.

The SAFT-VR theory was used to model the experimental results. The data are quantitatively reproduced by this approach,

**TABLE 4**SAFT-VR model parameters used in this work. The energy parameters  $\varepsilon$  and  $\varepsilon_{ab}^{HB}$  are divided by the Boltzmann constant  $k_B$ .

	$m$	$\sigma/\text{nm}$	$\frac{\varepsilon}{k_B}/\text{K}$	$\lambda$	H-sites	e-sites	$\frac{\varepsilon_{ab}^{HB}}{k_B}/\text{K}$	$10^3 K_{ab}^{HB}/\text{nm}^3$
Water	1	0.30342	250.000	1.7889	2	2	1400.00	1.06673
1-Propanol	1.8667	0.37571	215.012	1.7019	1	2	2499.96	0.19621

with binary interaction parameters which are only slightly different from those previously obtained for the (water + ethanol) system.

### Acknowledgments

One of us (AFC) is grateful to Fundação para a Ciência e a Tecnologia (Portugal) for financial support under PhD grant SFRH/BD/48596/2008. PM acknowledges funding from Fundação para a Ciência e Tecnologia, in the form of a grant (No. SFRH/BPD/81748/2011).

This work was partially supported by project PEst-OE/QUI/UI0536/2011 and PEst-OE/QUI/UI0100/2011.

### References

- [1] D. Zudkevitch, Encyclopedia of Chemical Processing and Design, Marcel Dekker, New York 14 (1983) 431–483.
- [2] G.C. Straty, A.M.F. Palavra, J. Res. National Bureau of Standards 89 (1984) 375–383.
- [3] A.M.F. Palavra, W.A. Wakeham, M. Zalaf, Int. J. Thermophys. 8 (1987) 305–315.
- [4] W.M. Haynes, A.J. Kidnay, N.A. Olien, J. Hiza, Advances in Cryogenic Engineering 27 (1984) 919.
- [5] S. Ohe, Vapour Liquid Equilibrium Data at High Pressures, Elsevier, Tokyo, 1990.
- [6] A.F. Cristino, S. Rosa, P. Morgado, A. Galindo, E.J.M. Filipe, A.M.F. Palavra, C.A. Nieto de Castro, High-temperature vapour–liquid equilibrium for the water–alcohol systems and modelling with SAFT-VR: 1. Water–ethanol, Fluid Phase Equilib., 341 (2013) 48–53.
- [7] G.A. Ratcliff, K.C. Chao, Can. J. Chem. Eng. 47 (1969) 148–153.
- [8] T. Adrien, S. Oprea, G. Maurer, Fluid Phase Equilib. 132 (1997) 187–203.
- [9] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, Fluid Phase Equilib. 52 (1989) 31–38.
- [10] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 1709–1721.
- [11] I.G. Economou, Ind. Eng. Chem. Res. 41 (2002) 953–962.
- [12] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, J. Chem. Phys. 106 (1997) 4168–4186.
- [13] A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, Mol. Phys. 93 (1998) 241–252.
- [14] H. Zhao, C. McCabe, J. Chem. Phys. 125 (2006) 4504–4515.
- [15] Isabel M.S. Lampreia, Carlos A. Nieto de Castro, J. Chem. Thermodyn. 43 (2011) 537–545.
- [16] G.C. Benson, O. Kiohara, J. Sol. Chem. 9 (1980) 791–804.
- [17] L.F. Vega, G. Jackson, Fluid Phase Equilib. 306 (2011) 1–3.
- [18] B. Patel, PhD. Thesis, Imperial College, London, 2004.
- [19] G.N.I. Clark, A.J. Haslam, A. Galindo, G. Jackson, Mol. Phys. 104 (2006) 3561–3581.
- [20] N. Mac Dowell, F. Llovel, C.S. Adjiman, G. Jackson, A. Galindo, Ind. Eng. Chem. Res. 49 (2010) 1883–1899.
- [21] P. Susial, J.C. Apolinario, J.J. Rodríguez-Henríquez, V.D. Castillo, E.J. Estupiñán, Fluid Phase Equilib. 331 (2012) 12–17.
- [22] W. Wagner, A. Kruse, Properties of Water and Steam, Springer-Verlag, Berlin, Germany, 1998.

JCT 12-637